A Potential Model for Chemical Oscillations

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Abstract

Oscillation characteristics: induction period, oscillation period, peak potential, and total oscillation time of Belousov-Zhabotinsky systems, which consisted of bromate - oscillator [Ce^{4+} or Mn^{2+} or ferroin] - malonic acid were deter- mined using SCE/Pt and Cu/Pt electrodes. The solution potential requirements for appearance of chemical oscillations were determined by finding the concentra- tion limits of the reactants, bromate and malonic acid, and measuring the corres-ponding solution reduction potentials. A chemical oscillation model was proposed.

***Keywords**: Chemical oscillation, Belousov-Zhabotinsky systems, cerium (IV) manganese (II), ferroin, potential requirements, oscillation mode.*

Introduction

The continuous and alternate oxidations and reductions of an oscillator, which makes it "flip-flop" between its oxidized and reduced states, are responsible for chemical oscillations (Win 1978). Induction period, *tin*; oscillation period or time between two consecutive oscillation peaks, *tos;* peak potential, *pp;* peak width, *fwhm;* and total oscillation time, *tot* are normally used for characterization of chemical oscillations (Win and Win 1985, Win 2001)

The most extensively studied liquid phase homogenous oscillation system is the Belousov-Zhabotinsky oscillation. It consists of an oxidant (usually bromate ion), a reductant (an organic compound containing hydrogen atoms, α to a carbonyl group, such as malonic acid) and an oscillator - a metal ion which can easily be inter-converted between its oxidized and reduced states, such as Ce^{3+} /Ce^{4+}.

Chemical oscillation systems are composed of two opposing reactions: an oxidation reaction consisting of bromate and reduced oscillator, such as Ce^{3+}, Mn^{2+}or ferroin [iron(II)-1,10-phenanthroline]; and a reduction reaction consisting of malonic acid and oxidized oscillator, such as Ce^{4+}, Mn^{7+}, or ferriin [iron (III)-1,10-phenanthroline].

The oxidation and reduction reactions occur alternately; and effectively cause the oscillator to "flip-flop" between its reduced and oxidized states. For example in the three oscillation systems considered in this work: Ce^{3+}/Ce^{4+} in the bromate-Ce^{4+}-malonic acid system; Mn^{2+}/Mn^{7+} in the bromate - Mn^{2+}-malonic acid system; or ferroin / ferriin in the bromate - ferroin - malonic acid system.

Requirements of relative reaction rates of oxidation and reduction reactions for occurrence of chemical oscillations had been discovered (Aye 1988).

The present work determined solution potential requirements or conditions for the appearance of chemical oscillations by finding the concentration limits of the reactants: (bromate and malonic acid) for occurrence of chemical oscillations followed by measurement of the corres-ponding reduction potentials. A simple model was proposed.

Varied international interest is noted: such as interest in the phenomena (Hudson and Mankin 1981); interest in three dimensional models (Field and Gyoergi 1991, 1992); publication of books (Epstein and Pojman 2000); theoretical calculations

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(Martin 2001), and experimental observations (Olexova *et al.*1996).

Experimental

Potassium bromate, malonic acid, manganese (II) sulfate (VI), iron (II) sulfate (VI), ammonium cerium (IV) sulfate, 1.5 M sulfuric (VI) acid and 1,10-phenanthroline were of reagent grade (BDH), and used without further purification.

Standard solutions of various reagents were prepared by dissolving accurately weighed amounts of the above chemicals in exactly measured volumes of 1.5 M sulfuric (VI) acid, except for ferroin solutions which were prepared with deionized water.

A Corning pH meter was used in conjunction with platinum Pt, copper Cu and standard calomel SCE electrodes. The detailed procedure was as described previously (Win 2001).

Results and Discussion

Solution Potential Limits

For the Bromate - cerium (IV) - malonic acid system, the bromate concentration limits for occurrence of chemical oscillations were as shown in Table 1. Similar limits were found for malonic acid as shown in Table 2.

The solution reduction potentials of various solutions of bromate, malonic acid and oscillators: Ce^{4+}, Mn^{2+} and ferroin, were measured and shown in Table 3. It was found that the SCE/Pt values were lower than the corresponding Cu/Pt values. Since only relative potentials and variations were of importance and not the accurate absolute potentials, Cu/Pt measurements were equally useful as the accurate SCE/Pt measurements.

The Nernst equation, shown below, predicted that the reduction potentials should increase with increased concentrations of oxidized species (BrO_3^-) and decrease with increased concentrations of reduced species (malonic acid). Table 3 showed that this was true. The reduction potentials were raised with increased bromate concentrations and lowered with increased malonic acid concentrations.

$$E = E^{O} - 0.591/n \{\log [\text{reduced}]/[\text{oxidized}]\}$$

As seen in Table 3, concentration variations were accompanied by corresponding potential changes. Thus the concentration limits had corresponding potential limits for the occurrence of chemical oscillations. For example the bromate concentration limits, Table 1, were 0.02 M and 0.22 M; and the corresponding potential limits were 1134 mV (SCE/Pt), 1149 mV (Cu/Pt) and 1188 mV (SCE/Pt), 1197 mV (Cu/Pt), respectively.

The malonic acid concentration limits, Table 3, were 0.20 M and 1.60 M; and the corresponding potential limits were 450 mV (SCE/Pt), 470 mV (Cu/Pt) and 371 mV (SCE/Pt), 397 mV (Cu/Pt), respectively.

The concentration limits for the oscillators, which were present in minute amounts only, were difficult to determine. A constant concentration of 0.0006 M was used for all three oscillators. The corresponding potentials were shown in Table 3.

The Chemical Oscillation Model

At the start, the oscillator could be in the reduced oxidation state ($Mn^{2+}$and ferroin) or in the oxidized state (Ce^{4+}) depending on which of the three systems were used. Thus during the initial stages the former would be oxidized and the latter would be reduced. Appearance of the oxidized forms of the oscillator in the former and reduced forms of the oscillator in the latter, would set up reactions opposed to the initial oxidation or reduction. For example, initial Ce^{4+} reduction would produce $Ce^{3+}$and set up an oxidation reaction in opposition to the above initial reduction.

Rate adjustments would occur and they would be accompanied by corresponding potential changes. The adjustments would proceed until the two rates were appropriately close enough for oscillations to occur. A range of such appropriate

relative rates existed for every oscillation system (Aye 1988). The corresponding potential range was named the *critical potential range*.

A certain time interval would be necessary for the system to adjust its potential, *system potential*, to fall within the critical potential range. This would account for the existence of an induction period. The equilibrium system potential that falls within the *critical potential range* was called the *balance point potential*.

The *mid-point potential* was the average of bromate and malonic acid potentials. The system potentials values were shown in Table 4. The amplitude potential, consisting of a minimum and a maximum, showed the size of the oscillation waves around the stabilized section of oscillation traces. These sections usually start five minutes after onset of oscillations.

Due to the inorganic nature of bromate and the organic nature of malonic acid, the bromate oxidation would be faster than the malonic acid reduction. Thus the equilibrium potential or the balance point potential should be biased towards the bromate potential (higher potential) i.e. the balance point potential must be higher than the mid-point potential.

Also, bromate could not oxidize any chemical system with a more positive potential than itself. Hence all balance point potentials should be between the bromate and mid-point potentials. This was observed in Table 4. For example, at 0.02 M bromate the balance point potential was 966 mV (SCE/Pt), 982 mV (Cu/Pt) which was between bromate potential 1134 mV (SCE/Pt), 1149 mV (Cu/Pt), shown in Table 3; and mid-point potential 802 mV (SCE/Pt), 822 mV (Cu/Pt) shown in Table 4.

Based on the above facts a chemical oscillation model could now be established, as shown in Fig. 1.

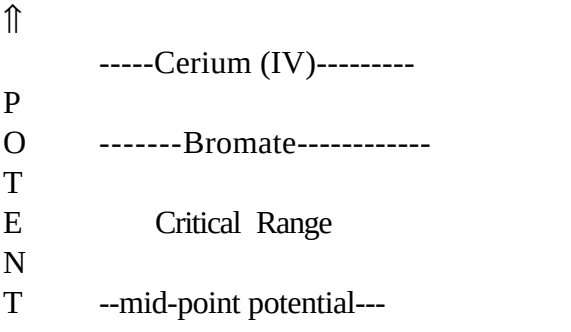

Fig. 1. Oscillation model.

Variations in bromate and malonic acid concentrations would induce system potential shifts, which also shifts the equilibrium potential or balance point potential.

The shift could be towards the critical range, the range within which oscillations would occur if the system equilibrium potential (balance point potential) fell within it; or it could be away from the critical range. The former would lead to shorter induction periods and the latter would lead to longer ones.

Another result of the bromate or malonic acid concentration variation was the potential difference between bromate and cerium (III) or malonic acid and cerium (IV). The former would occur if bromate was varied and the latter would occur if malonic acid were varied. These variations would affect the induction period in an opposite manner to the above system potential change.

For example, if malonic acid was increased, the malonic acid potential would move down. The system potential and the mid-point potential, the mid-way potential enclosed by the bromate and malonic acid potentials, would also move down. It would take longer for the system to equilibrate and place the balance point potential within the critical range. Consequently the onset of oscillations would be delayed. The induction period would be longer. For convenience this effect was named the system potential effect.

Another effect of increased malonic acid was the enhanced potential difference between malonic acid and cerium (IV) that would accelerate the reaction rate and cause shorter induction periods. This effect was named the rate effect.

The reverse effect should occur with bromate increases. Experimental expression of these two effects on the induction period would depend on their relative strengths.

As mentioned before, bromate reaction would be much faster than malonic acid. Thus the

rate effect should be predominant in the former and not in the latter. Thus, induction periods should increase with increased malonic acid; and also with increased bromate. This was substantiated for bromate in Table 1, where roughly, a 200% increase in induction period (540s to 1577s, SCE/Pt) was observed for an eight-fold increase in bromate. An increase of about 100% increase in induction period for a similar eight fold increase in malonic acid was seen in Table 2.

Longer induction periods would indicate the increased difficulty of the system potential adjustment to place the balance point potential within the critical range. For such conditions, the balance point potential would only be barely inside the critical range. Consequently the oscillations should not last long and the amplitude of the oscillation waves should be minimized.

This was experimentally found for bromate in Table 1, where the lower bromate limit had an induction period of 540 s (SCE/Pt), 556 s (Cu/Pt); oscillation period of 74 s (SCE/Pt), 68 s (Cu/Pt); peak potential 77 mV (SCE/Pt), 64 mV (Cu/Pt) as compared to the corresponding values for the upper bromate limit: induction period 1577 s (SCE/Pt), 1567 s (Cu/Pt); oscillation period 28 s (SCE/Pt), 29 s (Cu/Pt); peak potential 14 mV (SCE/Pt), 9 mV (Cu/Pt). A similar trend was found for malonic acid in Table 2.

Thus the model was adequate to describe the qualitative aspects of chemical oscillations and would complement the more complicated two major mathematical models of chemical oscillations: the Oregonator and the Brusselator (Tyson 1985).

Similar data, which supported the discussions presented here, were observed for the other two oscillation systems: bromate-Mn^{2+}-malonic acid system and the bromate-ferroin-malonic acid system (Than 1988).

Conclusion

During the initial stages the oscillator would be first oxidized, if in the reduced state (ferroin and Mn^{2+}) or reduced, if in the oxidized state (Ce^{4+}). These would produce ferriin and Mn^{7+}or Ce^{3+}, and set up an opposing reaction. At equilibrium the oxidation and reduction rates would be equal. At near-equilibrium conditions, a condition could be achieved where the two rates would increase and decrease alternately in

opposition to each other. The oscillator would then be oscillating between its oxidized and reduced states.

Ideally the initial oscillator potential should be between the bromate and malonic acid potentials. However oscillations could still be observed if the initial oscillator potential was outside, but not too far removed from the range enclosed by the bromate and malonic acid potentials.

References

Aye, M.M. 1988. Rate requirement for occurrence of chemical oscillations. M.Sc. Thesis. Yangon University, Yangon, Myanmar.

Field, R. J.; and Gyoergi, L. 1992. A three-variable model of deterministic chaos in the Belousov-Zhabotinsky reaction. *In:* Letters to Nature. Nature 355: 808-10.

Field, R. J.; and Gyoergi, L. 1991. Simple Models of Deterministic Chaos in Belousov - Zhabotinsky Reaction. J. Phys. Chem. 95: 6594-602.

Epstein, I. R.; and Pojman, J. A. 2000. An introduction to nonlinear chemical dynamics: Oscillations, waves, patterns, and chaos. J. Chem. Educ. 77: 450.

Martin, S.T. 2001.Employing Complex Kinetic Diagrams. Math.J. 8: 1-20.

Olexova, A.; Melichercik, M.; and Treindl, L. 1996. Permanganate chemical oscillators with cyclic diketones. Collect. Czechoslovak Chem. Comm. Abstracts: 61(1): 70-6.

Than, M.M. 1988. Potential requirement for occurrence of chemical oscillations. M.Sc. Thesis. Yangon University, Yangon, Myanmar.

Tyson, J.J. 1985. Oscillations and traveling waves in Chemical Systems. Wiley, New York, pp. 93-144.

Win, D.T. 2001. A six-sensor for testing ambient air quality. AU J.T. 4: 157-63.

Win, D.T.; and Win, S. 1985. Chemical Oscillations. CRT Project Report I. Univ. of New South Wales, Sydney, Australia.

Win, Y. Y. 1978. Nature of chemical oscillations. M. Sc. Thesis. Yangon University, Yangon, Myanmar.

Table 1. Effect of varying bromate concentration on oscillation characteristics
[Bromate-cerium(IV)-malonic acid system]

[Bromate] / mol L^{-1}	**SCE/Pt**			**Cu/Pt**		
	***tin*/s**	***tos*/s**	***pp*/mV**	***tin*/s**	***tos*/s**	***pp*/mV**
0.02	540	74	77	556	68	64
0.06	695	46	54	743	44	45
0.10	883	40	46	924	40	35
0.14	1125	33	34	1140	34	22
0.18	1577	28	14	1567	29	9

Table 2. Effect of varying malonic acid concentration on oscillation characteristics
[Bromate-cerium(IV)-malonic acid system]

[Malonic Acid] / M	**SCE/Pt**			**Cu/Pt**		
	***tin*/s**	***tos*/s**	***pp*/mV**	***tin*/s**	***tos*/s**	***pp*/mV**
0.20	360	13	55	396	14	43
0.80	380	6	36	452	6	28
1.20	490	5	21	538	5	18
1.60	715	4	8	750	4	6

Table 3. Potentials of Various Solutions

Solution	**Concentration/M**	**Reduction Potential / mV**	
		SCE/Pt	**Cu/Pt**
Bromate	0.02	1134	1149
	0.06	1162	1173
	0.10	1175	1190
	0.14	1180	1193
	0.18	1186	1195
Malonic	0.20	450	470
Acid	0.80	400	431
	1.20	383	411
	1.60	371	397
Ce^{4+}	0.0006	1174	1189
Mn^{2+}	0.0006	474	510
Fe^{+2}	0.0006	430	467

Table 4. Oscillation System Potentials

Bromate Conc. / M	Amplitude Potential/mV		Balance-point Potential/mV		Mid-point Potential/mV	
	SCE/Pt	Cu/Pt	SCE/Pt	Cu/Pt	SCE/Pt	Cu/Pt
0.02	927-1004	950-1014	966	982	802	822
0.06	970-1024	986-1031	997	1009	816	834
0.10	1015-1061	1023-1058	1033	1041	823	843
0.14	1046-1080	1051-1073	1063	1062	825	844
0.18	1087-1101	1089-1098	1094	1094	828	845